

# Chapter 2

## UNUSUAL SEED OILS AND THEIR FATTY ACIDS

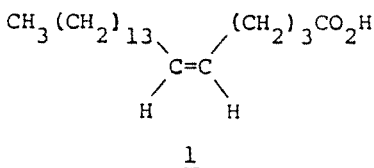
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### INTRODUCTION

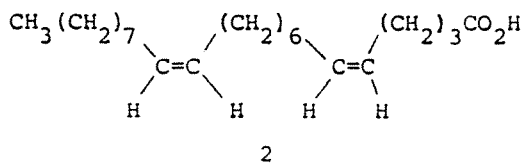
Many agricultural scientists in various parts of the world look for practical uses for plants that are not presently in cultivation. Favorite objects of such investigations have been oils and fats, especially those produced by seeds of flowering plants. The Agricultural Research Service, U.S. Department of Agriculture, has carried on an extensive program of research aimed at discovering new seed oils and fatty acids which may lend themselves to practical utilization. At the same time, investigators in other countries have conducted parallel investigations. The purpose of this chapter is to summarize the more important discoveries in this area. Among the points considered are structures of unusual fatty acids in prospective new oilseed crops; botanical and agronomic characteristics of the plants under discussion; distinctive reactions and synthesis of the unusual fatty acids; and characteristics of the residual meals after extraction of the oils. Coverage will be restricted to oilseeds which provide major amounts of unusual fatty acids and show some degree of promise in their crop potential. A more complete tabulation of unusual fatty acids from plants was given by the author in a chapter published in 1970 (1), and this was updated later by Hitchcock (2) and by Galliard (3). Parallel reviews in German (4,5) and in Japanese (6) have appeared.

### LIMNANTHES

Seed oils of the genus *Limnanthes* are probably unique in containing over 95% of fatty acids with chain lengths greater than  $C_{18}$ , including 63% 20:1, 18% 22:1, and 13% 22:2 (7-10). The double bond is in the 5-position in most of the 20:1 (1) and in a portion of the 22:1. The 22:2 is *cis*-5,*cis*-13-

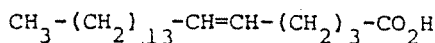
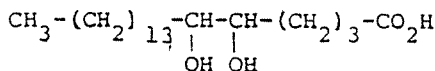
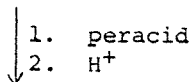
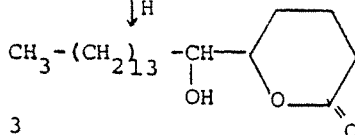
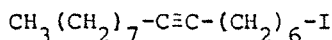
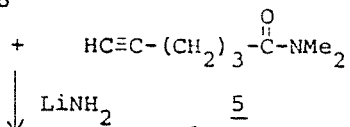
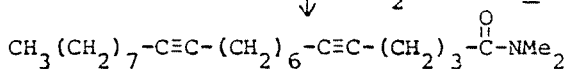
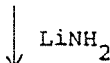
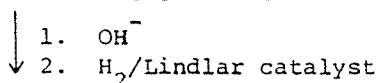


docosadienoic acid (2).

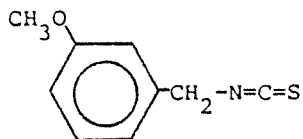
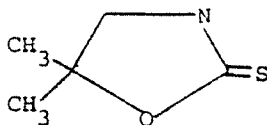


*Limnanthes* seed oils have been suggested as sources of cleavage acids, of solid waxes, and of liquid ester waxes with properties similar to those of sperm whale oil (11,12). Liquid waxes can be prepared from limnanthes oil in a one-step hydrogenation process with a copper chromite catalyst. Oxidative cleavage of 1, the predominant fatty acid of limnanthes, yields glutaric and pentadecanoic acids. The latter C<sub>15</sub> acid is not commonly available on the commercial market. Fore and Sumrell (13) observed that 1 can be converted by conventional epoxidation procedures to a diol (1a) which can be cyclized to a novel hydroxylactone (3). Fore, Dollear, and Sumrell (14) as well as Chang and Rothfus (15) reported procedures for isolating 2 in an enriched form. This unusual dienoid acid with its widely separated double bonds would be expected to undergo transformations into bifunctional derivatives, e.g., diepoxides, more smoothly than conventional methylene-interrupted acids. Acid 2 has been synthesized by Ames, Covell, and Goodburn (16). They condensed 1-iodohexadec-7-yne (4) with *N,N*-dimethylhex-5-ynamide (5) in the presence of lithium amide to give a diynoic acid (6). After alkaline hydrolysis of 6 and semihydrogenation with Lindlar catalyst, 2 was isolated.

*Limnanthes* (family Limnanthaceae) is a genus of winter annual, herbaceous plants native to the West Coast of the USA (17,18). Some varieties have good agronomic characteristics and appear to have considerable potential as field crops. The protein content and amino acid composition of the oil-free limnanthes meal suggest that it would be a good protein supplement for livestock since the lysine and methionine levels are relatively high (19). However, limnanthes seeds contain

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glucosinolates, a class of compounds usually associated with the Brassicaceae (e.g., crambe, rapeseed); these compounds could be detrimental to the quality of limnanthes meal. Upon hydrolysis, the glucosinolate of *L. douglasii* seed oil yields *m*-methoxybenzyl isothiocyanate (7), a volatile mustard oil

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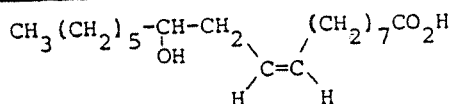
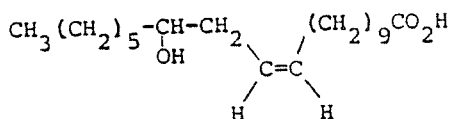
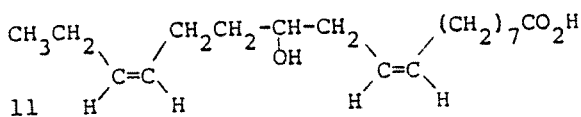
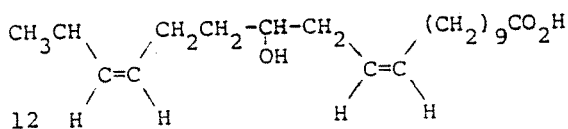
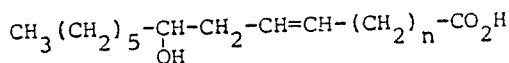
which could be easily removed by processes applied to mustard seed (10). However, in addition to 7, glucosinolates of *L. alba* also yield a goitrogenic non-volatile hydrolysis product, 5,5-dimethyloxazolidine-2-thione (8) (20). Calhoun and co-workers at Oregon State University have undertaken a program of cultivating, breeding, and developing limnanthes as a new crop for the Pacific Northwest (21). Similar efforts in Maryland and California are underway.

### LESQUERELLA

Seed oils of the genus *Lesquerella* resemble castor oil more than they do others of the plant family Brassicaceae to which they belong. Three hydroxy acids related to ricinoleic acid (9) occur in major amounts in oils from various *Lesquerella* species. Lesquerolic acid (10) is a  $C_{20}$  homolog of 9 with two additional carbons at the carboxyl end of the chain (22). Densipolic acid (11) differs from 9 in having an extra double bond in the terminal portion of the carbon chain (23). The most recently discovered, auricollic acid (12), incorporates features of both 10 and 11 (24). *Lesquerella* species are divided into three groups, each of which produces 10, 11, or 12 as its predominant hydroxy acid, usually to the exclusion of the other two acids (24,25).

Ricinoleic acid (9) undergoes various cleavage reactions to give products which are standard items of commerce. Lesquerolic acid (10) would be expected to give analogous products under similar conditions, and this has been verified in the case of the alkaline cleavage reactions (26,27). In the presence of sodium hydroxide above  $250^{\circ}\text{C}$ , 10 gives a high yield of dodecanedioic acid (13,  $n = 9$ ) and (+)-octanol-2 (14). At somewhat lower temperatures ( $180$ - $250^{\circ}\text{C}$ ), 10 provides 12-hydroxydodecanoic acid (15,  $n = 9$ ) and octanone-2 in the presence of alkali. The yields in the latter reaction are lower than in the higher temperature alkaline cleavage. The mechanism of these reactions has been discussed by Diamond, Binder, and Applewhite (27).

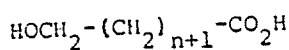
In the absence of acid or base, ricinoleic acid (9) undergoes a thermal fragmentation, probably by a concerted mechanism (28), to give heptanal (17) and 10-undecenoic acid (18,  $n = 8$ ). The analogous products from lesquerolic acid (10) would be 12-tridecenoic acid. Similarly, 10, 11, and 12 would be expected to furnish a wide range of derivatives analogous to those from ricinoleic acid (9), including products of dehydration, oxidation, hydrogenation, and derivatization of hydroxyl and/or carboxyl functions (29,30). However, these various derivatives from the *lesquerella* acids will have physical properties different from those of ricinoleic acid so

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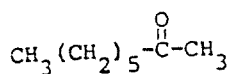
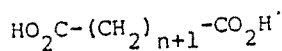
9, n = 7  
10, n = 9

NaOH  
 180-250°C

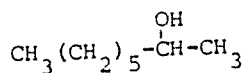
NaOH, 250°C

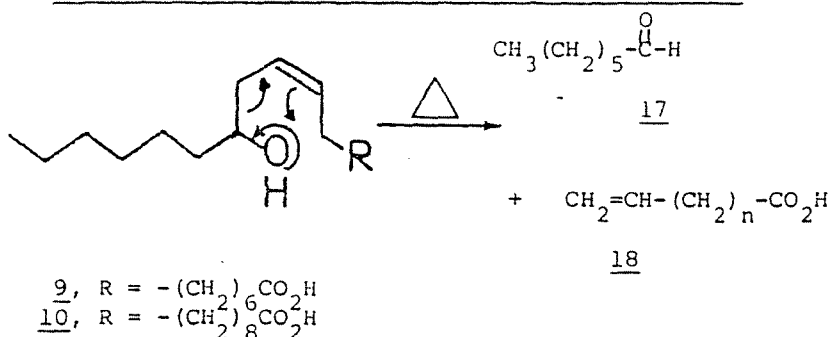
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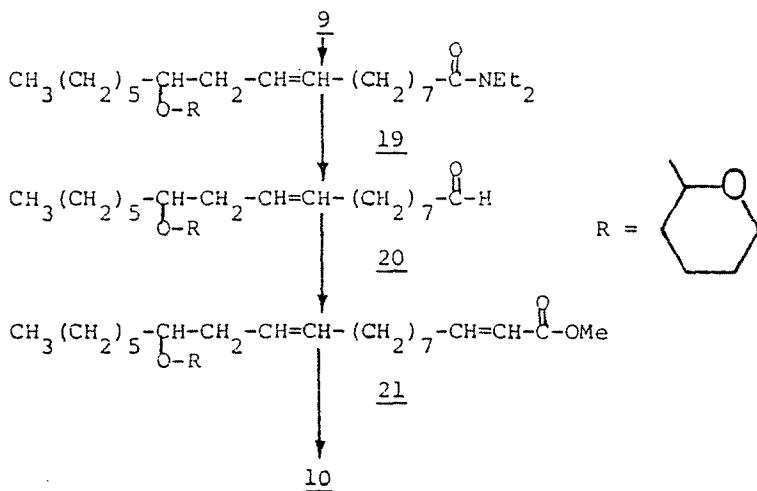
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that they may lend themselves to different applications in making plastics, lubricants, and other industrial products.

Lesquerolic acid (10) has been synthesized by Applewhite through a procedure in which he homologated ricinoleic acid and thereby confirmed the close relationship between the two (31). Acid 9 was converted to its diethylamide derivative, and the hydroxyl was protected with dihydropyran. The intermediate (19) thus provided was converted to an aldehyde (20) by treatment with lithium triethoxyaluminumhydride. At this stage, two carbons were added to the chain by a Wittig-type condensation of (20) with the anion of triethylphosphonate to give an  $\alpha,\beta$ -unsaturated ester (21). Selective reduction of 21 with sodium in *n*-butanol provided 10.

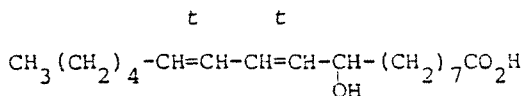


*Lesquerella* is a genus of winter annual or perennial herbs which are widely distributed in Western North America and to a limited extent elsewhere. Some species have characteristics which are favorable for development of an annual field crop (32). Good progress has been made in improving problems of seed dormancy and prostrateness on wild-type *L. fendleri*; breeding efforts are now centered on improving seed shattering characteristics (personal communication from D. D. Rubis, University of Arizona, 1977). The composition of *lesquerella* seed oils raises the prospect of a domestic source of a castor-like oil from an annual field crop which would reduce dependence on imports.

Economic development of *lesquerella* as a field crop will require attention to characteristics of the residual meal as a potential feedstuff. Like other members of the crucifer family, *lesquerella* seeds contain glucosinolates which must be evaluated in terms of their impact on animal nutrition and processing technology (33). *Lesquerella lasiocarpa* is the original natural source of 6-thiomethylhexyl glucosinolate (34). Enzymatic hydrolysis of this compound under proper conditions produces a volatile isothiocyanate which should be easily removed in processing. Some cruciferous meals contain glucosinolates that give rise to goitrogenic substances (thio-oxazolidones) (35,36); none of these occur in *lesquerellas* (33). The amino acid composition of meals from 14 *lesquerella* species has been determined (37), and their high lysine content suggests that they may be good protein supplements for feed grains.

#### DIMORPHOTHECA

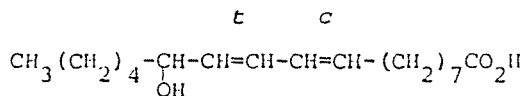
Dimorphecolic acid (22) was first isolated from the seed oil of *Dimorphotheca sinuata* (family Compositae) (38). Acid 22 represents 65-67% of the seed oil of this species (38,39),



22

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and also is the predominant fatty acid in oils from other *Dimorphotheca* species as well as certain species of the related genera *Osteospermum* and *Castalis* (40). Dimorphecolic acid is the prototype of a class of fatty acids with a distinctive conjugated dienol grouping. Coriolic acid (23), discovered



23

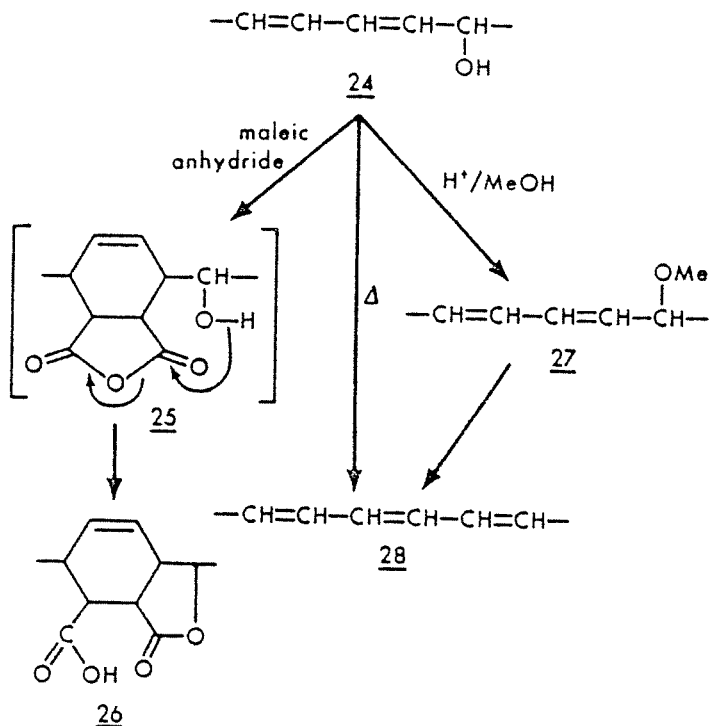
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subsequently as a major constituent of *Coriaria nepalensis* (family Coriariaceae) seed oil, is a geometric and positional isomer of 22 (41). Minor proportions of 22 and 23, or their geometric isomers, occur in seed oils of numerous species of the plant family Compositae. These acids have an obvious structural relationship to the hydroperoxides derived from linoleic acid by the action of lipooxygenases or by autooxidation, but they are not artifacts of isolation (42). Moreover, 22 evidently is not formed by the lipooxygenase which was isolated from dormant *D. sinuata* seed, since the hydroperoxide produced by that enzyme differs from 22 in position and configuration of the oxygen function and in geometry of double bonds (43).

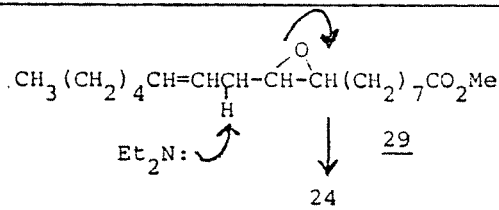
Dimorphecolic acid confers some unusual properties upon dimorphothea oil that make it particularly versatile among vegetable oils in its chemical reactions. After suitable processing, dimorphothea oil affords a drying oil comparable to the product from tung in its film-forming properties (44-46). Methyl dimorphecolate (24, shown in abbreviated format), with its two *trans* double bonds in conjugation, readily undergoes the Diels-Alder reaction with reactive dienophiles such as maleic anhydride. Because of its  $\alpha$ -hydroxy group, 24 gives an abnormal adduct in which the anhydride grouping (as in 25, a probable intermediate) rearranges to give an  $\alpha$ -carboxy- $\gamma$ -lactone (26) (38). Dimorphecolic acid (as a methyl ester, triglyceride, or other esterified form) is readily dehydrated to give an all-*trans* conjugated triene (28) (38,42,44,46). In acidic methanol solution, 24 is dehydrated under quite mild conditions through an intermediate methyl ether 27 (42). This exceptional reactivity is due to the allylic character of the hydroxyl group in 24 reinforced by a second double bond in conjugation. A comparable reaction occurs when 23 (or its esters and glycerides) are treated with hydrogen bromide; this reaction is so rapid that it provides the basis for an analytical titration of conjugated dienols (47-50). Methyl dimorphecolate *per se* undergoes thermal dehydration with such facility that it is difficult to analyze by GLC; this difficulty is readily overcome by silylation before GLC to protect the hydroxyl function (51).

Methyl dimorphecolate and methyl coriolate have been synthesized by Conacher and Gunstone (52) from methyl esters





of the related epoxy acids, coronaric (29) and vernolic acids. Under the influence of lithium diethylamide, 29 undergoes a  $\beta$ -elimination reaction to give 24. Methyl coriolate was prepared similarly from methyl vernolate.

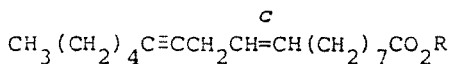


A limited agronomic evaluation of several species of *Dimorphotheca* and *Osteospermum* has been carried out (53,54). These plants have characteristics that provide the potential for development of a new annual oilseed crop. However, considerable selective breeding would be required to develop varieties suitable for cultivation; in particular, disease

resistance and seed retention need improvement (54). Dimorphotheca seeds are high in oil and crude protein, although the proportions of lysine and methionine in that protein are relatively low (19).

#### CREPIS

Crepenynic acid (30) was isolated originally from seed oil of *Crepis foetida* in which it occurs to the extent of 60% (55). Bohlmann et al. (56) remarked that crepenynic acid



30a, R = H

30b, R = Me

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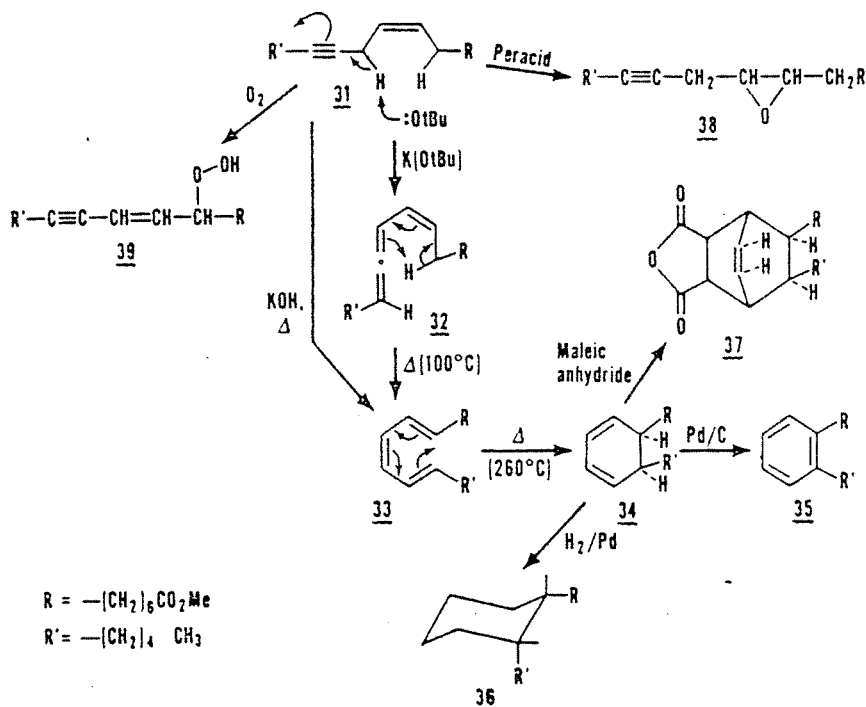
is "perhaps the most important acetylenic fatty acid." Widespread interest in the biochemistry of this acetylenic analog of linoleic acid has been evidenced in several ways. The biogenesis of 30 has been examined (57,58), and there have been experimental studies, as well as speculations regarding its rôle in the biosynthesis of more highly unsaturated acetylenes (58-61). The metabolic fate of 30 has been studied in rats (62).

The genus *Crepis*, a member of the family Asteraceae, comprises about 200 species widely distributed throughout the world (63). A survey of oils from representative *Crepis* species indicated that some contain high levels of crepenynic acid while others have epoxy acids instead; certain species produce a combination of both (63,64). Crepenynic acid also has been found in seed oils of other genera (65).

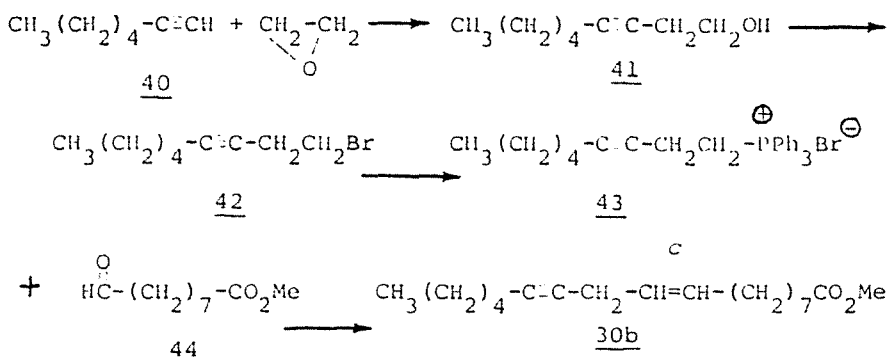
The unique chemistry of crepenynic acid makes it a potential source of cyclic acids, either saturated or aromatic, for low-temperature lubricants. Under the influence of alkali and/or heat, methyl crepenynate (31) undergoes an intriguing series of rearrangements; 31 is isomerized to an eneallene (32) by potassium t-butoxide at ambient temperature. At 100°C, 32 undergoes a thermal rearrangement to give a previously unknown *trans*-8,*cis*-10,*trans*-12 triene (33) with lesser amounts of other conjugated triene isomers (66,67). At a higher temperature (260°C), 33 is cyclized to give a cyclohexadiene derivative (34). Although the stereochemistry of the two ring substituents in 34 was not established in the

original investigation, they must be *cis* in accord with the Woodward-Hoffmann rules for electrocyclic reactions (68). Cyclodiene 34 can be aromatized to give 35 or hydrogenated to furnish a saturated cyclic acid (36); 34 also provides a Diels-Alder adduct (e.g., 37) when treated with maleic anhydride or other reactive dienophiles (67). Cyclic acids such as 36 are potential low-temperature lubricants (69).

Triple bonds are rather resistant to the action of peroxy acids. Consequently, when methyl crepenynate is reacted with *m*-chloroperoxybenzoic acid, it is readily converted into a monoepoxide (38) in which the acetylenic linkage is preserved (55,65). Structure 31 yields an autoxidation product analogous to the familiar linoleate hydroperoxide (51), but with a conjugated enyne structure.



Jones and his associates at Oxford have synthesized crepenynic acid in at least three ways (70-72), all based on acetylene coupling reactions. In the sequence illustrated in the accompanying reaction scheme (71), 1-heptyne (40) was condensed with ethylene oxide by lithium in liquid ammonia to give 3-nonyn-1-ol (41). Alcohol 41 was converted to the corresponding bromide (42) by treatment with phosphorus tri-bromide, and then to a triphenylphosphonium bromide (43) by reaction with triphenylphosphine. Bromide 43 was condensed with an aldehyde-ester (44) through a Wittig reaction to give methyl crepenynate (30b).



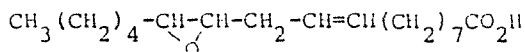
*Crepis* is native to Eastern Europe and the Middle East. Little agronomic development work has been done on *Crepis*, although *Crepis alpina* is considered to have the best crop potential of the species tested as a crepenynic acid source (73). The amino acid composition of *C. foetida* and *C. vesicaria* indicates that their proteins are fairly high in their content of lysine and methionine (74).

#### EPOXY OIL SOURCES

Potential industrial interest in epoxidized oils from natural sources is derived largely from the demand for chemically epoxidized vegetable oils. In particular, soybean oil is epoxidized at the rate of 77 million lbs annually and this product commands a price of \$0.44 per pound, roughly \$0.24 more than regular soybean oil (1975 figures; ref. 75). Replacement of epoxidized soybean oil with a biosynthetically produced epoxy oil would effect a considerable energy saving.

Fatty acids with epoxy groups occur naturally in seed oils of a considerable number of plant species, and are major constituents in several cases. The first seed oil of this

group to be investigated was that of *Vernonia anthelmintica* (76); its characteristic epoxy acid, vernolic acid (45), is the most familiar and widely distributed of the natural epoxy fatty acids. A number of additional epoxy acids were discovered subsequently in seed oils (1-3,77-81).



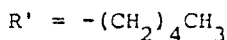
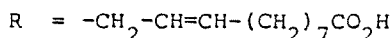
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In principle, vernolic acid and related epoxy acids may undergo any reaction exhibited by the oxirane group; only a few of the most characteristic examples are summarized in the accompanying reaction scheme. (+)-Vernolic acid (45) is transformed into a (-)-threo-diol (46) by acetolysis or, under moist conditions, into a (+)-threo-diol (46) by the action of an enzyme contained in *V. anthelmintica* seed; these two diols are optical antipodes (77). On treatment with a hydrogen halide, *p*-toluenesulfonic acid, an amine, or any nucleophilic reagent, 45 undergoes ring opening to give an addition compound; usually two isomers (e.g. 47 and 48) are formed. Reduction by catalytic hydrogenation or by lithium aluminum hydride gives two isomeric monohydroxy derivatives (49 and 50). Performance of oils with a high content of vernolic acid, also of some vernolate esters, as plasticizers and stabilizers for polyvinyl chloride was investigated with favorable results (77,82,83).

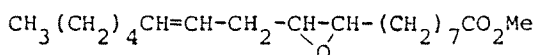
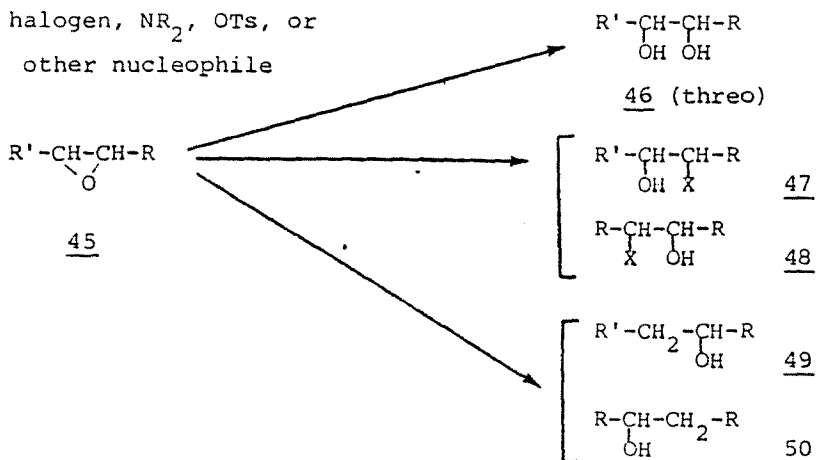
(+)-Methyl vernolate and the isomeric (+)-methyl coronate (51) are produced as a mixture of monoepoxidation of methyl linoleate (84). To the author's knowledge, no stereospecific or regiospecific syntheses of these epoxy acids have been published.

In terms of seed oil composition and crop potential, the most promising prospective sources of high epoxy oils are *Vernonia anthelmintica* (77,85), *Stokesia laevis* (77), and *Euphorbia lagascae* (86). A number of other genera are available, however, that produce high epoxy seed oils (79).

The seed oil of *V. anthelmintica*, a member of the family Asteraceae, contains about 72% vernolic acid (79). Botanical characteristics of the plant, as well as compositional studies on its seed oil, have been reviewed by Krewson (77,85). In *V. anthelmintica* oil, vernolic acid is incorporated almost exclusively in trivernolins, a fact which may find practical application if enhancement of the epoxy content of this oil



X = halogen,  $NR_2$ , OTs, or  
other nucleophile



51

is desired (85). *V. anthelmintica* is an annual herbaceous plant with characteristics indicating that it could be developed as a field crop. K. J. Lessman and his associates at Purdue University conducted a research program in which mode of pollination, crossing techniques, inheritability of desirable crop traits, and improved breeding lines were studied (87-90). Further developmental breeding is needed, however. Pilot-plant-scale extraction and processing of *V. anthelmintica* seed has been carried out successfully by Krewson and coworkers in a small continuous solvent extraction plant. This experimental processing was successful and required only minor changes in equipment designed for soybeans (91,92). The amino acid composition of *V. anthelmintica* seed meal indicates that methionine and lysine would be limiting nutritionally (19).

*Euphorbia lagascae* (family Euphorbiaceae) produces seed containing 42-50% oil, of which 58-62% is vernolic acid (86).

This plant is native to Southern Spain, and has been studied agronomically less than *Vernonia*. It has grown well as an annual in a number of locations, but its seed retention characteristics need improvement (93). The amino acid composition of *E. lagascae* seed meal indicates a good level of methionine, although lysine might be limiting (74).

*Stokesia laevis*, another member of the family Asteraceae, produces an oil containing 74% vernolic acid (79). *Stokesia* is native to the U.S. and has a number of promising characteristics which may make it the best prospect for a high-epoxy oilseed crop (78). It is a perennial and could be harvested annually without damage to the plant.

### CONCLUSION

Thus, there are numerous prospective new oilseed crops which could provide seed oils with fatty acids of unusual structure. These oils could become the source of derivatives not afforded by seed oils from present commercial oilseed crops without extensive modification. Alternatively, they might provide currently obtainable products more economically. Commercial development of these unusual oilseed crops will require the concerted efforts of agronomists, plant breeders, and industrial concerns that are interested in the products. Some of these plants could be beneficial in areas of the U.S. that need alternative crops for diversification of their agricultural economy, or for local sources of high protein supplements for feeds. In these days of concern about energy savings, unusual oilseeds also represent an energy-conserving way of obtaining economically valuable chemical intermediates.

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